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INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2002P02127WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP 03/07141	International filing date (day/month/year) 03.07.2003	Priority date (day/month/year) 09.07.2002
International Patent Classification (IPC) or both national classification and IPC C23C28/02		
Applicant SIEMENS AKTIENGESELLSCHAFT et al.		

1. This International preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 9 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☒ Certain defects in the international application
 - VIII ☒ Certain observations on the international application

Date of submission of the demand 31.10.2003	Date of completion of this report 26.07.2004
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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/07141**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-9 as originally filed

Claims, Numbers

1-12 received on 21.06.2004 with letter of 17.06.2004

Drawings, Sheets

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/07141**

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).
(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	3,4,6-12
	No: Claims	1,2,5
Inventive step (IS)	Yes: Claims	
	No: Claims	3,4,6-12
Industrial applicability (IA)	Yes: Claims	1-12
	No: Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/07141

Re Item II

Priority

The priority of the subject-matter of claim 14 is not valid, since this subject-matter is not found in the original disclosure.

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The following documents are referred to in this communication; the numbering will be adhered to in the rest of the procedure:

- D1: PATENT ABSTRACTS OF JAPAN vol. 1997, no. 10, 31 October 1997 (1997-10-31) & JP 09 157866 A (MITSUBISHI HEAVY IND LTD), 17 June 1997 (1997-06-17)
- D2: SCHMITT-THOMAS K G ET AL: 'IMPROVED OXIDATION RESISTANCE OF THERMAL BARRIER COATINGS' SURFACE AND COATINGS TECHNOLOGY, ELSEVIER, AMSTERDAM, NL, vol. 120/121, 1999, pages 84-88, XP001004807 ISSN: 0257-8972
- D3: US-A-5 514 482 (STRANGMAN THOMAS E) 7 May 1996 (1996-05-07)
- D4: US 2001/004475 A1 (ALLEN WILLIAM PATRICK ET AL) 21 June 2001 (2001-06-21)
- D5: US-B1-6 291 084 (GRYLLS RICHARD JOHN ET AL) 18 September 2001 (2001-09-18)
- D6: EP-A-1 167 575 (GEN ELECTRIC) 2 January 2002 (2002-01-02)
- D7: US-B1-6 403 165 (LAU YUK-CHIU ET AL) 11 June 2002 (2002-06-11)
- D8: US-A-6 001 492 (JACKSON MELVIN ROBERT ET AL) 14 December 1999 (1999-12-14)
- D9: EP-A-0 718 419 (CHROMALLOY UK LTD ;ROLLS ROYCE PLC (GB)) 26 June 1996 (1996-06-26)

2.

2.1. The present application focuses on the protection of parts, which require a high oxidation resistance, such as blades or vanes of gas turbines. As an object it is stated "to describe a protective layer [i.e. layer between the substrate and the thermal barrier coating] with a good oxidation resistance and good bonding to the thermal barrier coating" (page 2, line 30 - 34).

2.2. To solve the problem it is suggested that the protective layer consists of two layers, an inner conventional MCrAlY layer and an outer layer consisting at least of the elements Ni and Al and possessing a β -NiAl structure and having an Al content in the range between 21 - 37 wt. %.

3. Prior art and novelty.

3.1. D1 discloses a coating imparting corrosion and oxidation resistance to parts exposed to a hot environment, e.g. gas turbines, boilers. The coating consists of an MCrAlY layer and a NiAl layer consisting of a single phase. The MCrAlY layer increases the adhesion with the base material and its uniformity. In examples 2 and 3 of table 2 of the Japanese laid open application and its computer translation from the Japanese patent office (both attached to this communication) a NiAl layer is deposited on top of a CoNiCrAlY layer. The NiAl layer of the examples has a composition of 50Ni-50Al (ex. 2) or of 56Ni-44Al (ex. 3), which corresponds to an Al content of 31.5 wt. % or 26.6 wt. %, respectively. These compositions have the structure of a β -NiAl phase (see attached Ni-Al phase diagram).

The translation further reveals that the MCrAlY layer has a composition in wt. % of Ni: 31 - 32, Cr: 20 - 33, Al: 7 - 9, Y: 0.25 - 0.65 and Co: balance (paragraph 0022). Further, a heat treatment is carried out after the layers have been deposited, namely at 1120°C to 2 h and at 843°C for 24 h (paragraph 0029). It is assumed that some metal of the MCrAlY layer diffuses at these conditions into the β -NiAl layer.

Hence, also claims 1,2 and 5 lack novelty over D1.

3.2. D2 also refers to coatings for parts of gas turbines. A triplex coating consisting of a CoNiCrAlY bond coat, a Pt-modified aluminide coating and an yttria-stabilized zirconia coating was investigated. In the as-coated Pt-aluminide coating there is an outer region of PtAl_2 and of (Co, Ni, Pt)Al followed by a single phase layer of (Co, Ni, Pt)Al (abstract). The (Co, Ni, Pt)Al layer has a β -structure (page 85, point 3.1.). The aluminide layer is thinner than the CoNiCrAlY bond layer (page 85, point 2.1.).

D2 is not prejudicial for novelty of claim 1 of the present application, since there is no

statement made about the amount of Al in the β -(Co, Ni, Pt)Al layer.

3.3. D3 teaches coatings for superalloy turbine engine components in which a diffusion aluminide layer is used as the bond coating for the thermal barrier coating (abstract). In col. 3, line 25 - 45, preparation of the aluminide coating is described. During reaction of the Al with the substrate inter alia NiAl is formed, which is known to possess a β -NiAl structure and which has an Al content of 31.5 wt. %. According to claim 17 a MCrAlY layer may be applied prior to aluminiding. Since no details are given how the Al is deposited onto the MCrAlY layer and how both layers are reacted, no statements can be made about phases formed or their Al content, if an MCrAlY layer is coated on the substrate before the aluminide is formed. Hence, D3 is not novelty-destroying for claim 1.

3.4. D4 discloses coatings for certain parts / portions of gas turbines. In [0030] and Fig. 4 an embodiment is described in which an aluminide layer is applied on an overlay coating on a substrate, e.g. a superalloy material. The overlay coating is an MCrAlY layer, which may have the compositions as laid out in [0025] and table 2. See also claims 1 - 5 and 11. Fig. 4 shows that the aluminide layer 30 is thinner than the overlay coating 24. Claim 1 of the present application is novel over D4, because D4 does not give any details about the aluminide (composition, structure). There is also no thermal barrier layer deposited on top of the aluminide coating.

3.5. D5, D6 and D7 all relate to parts of gas turbines, which are coated with a β -NiAl layer on top of which a thermal barrier layer is deposited. These documents clearly point out the advantages of β -NiAl as a bond coat layer. However, these documents are not prejudicial for novelty of claim 1, since there is no MCrAlY layer disclosed below the aluminide layer.

3.6. D8 discloses a graded bond coat for a thermal barrier coating for components used in a hostile environment, such as parts of gas turbines (abstract). The coating comprises at least three layers. The inward layer may be a MCrAlY layer; the outward layer contains a Cr phase and a Pt-containing phase such as (Pt, Ni) Al and (Ni, Pt, Cr, Al). Claim 1 is novel over D8, since no statements about the structure or the composition of these phases are made.

3.7. D9 discloses a thermal barrier coating for a super alloy article in which into a bond layer Pt is diffused to form an intermediate layer between said bond layer and the thermal barrier coating layer (abstract, page 1, line 23 - 39): In Figs. 2a and 2b separate

layers are shown, with the Pt aluminide layer being thinner than the bond layer. The bond layer may be a Ni or Co aluminide, but MCrAlY is preferred. The Pt aluminide layer contains at least 8 wt % of Al (page 2, line 7 - 14). In Example 9 it is mentioned that platinizing the MCrAlY layer according to the method disclosed in D6 forms a beta phase which is rich in (Pt, Co, Ni)Al (page 11, line 32 - 47). However, no statement is made about the Al content and therefore claim 1 is novel over D9.

4. Inventive step.

4.1. D1 does apparently not explicitly mention that a thermal barrier coating is formed on the aluminide layer. However, it is not considered to be inventive to have a substrate coated via a bond layer with a thermal barrier layer, in which the bond layer is characterized by consisting of a MCrAlY and a β -NiAl layer.

It is known to use a β -NiAl as a bond coat layer for thermal barrier coatings of parts of articles used in hostile environments, e.g. parts of gas turbines (D5 - D7). D1 discloses a coating for the same kind of parts in which a MCrAlY layer is inserted between the substrate and the β -NiAl layer. It is taught that the MCrAlY layer increases the adhesion with the base material and its uniformity. The skilled person would therefore consider to combine the teaching of D1 with the teaching of D5 - D7 to improve the adhesion of the NiAl layer on the substrate. Therefore, claim 11 lacks inventive step.

4.2. D6 mentions in [0010] that as its key feature the β -NiAl coating contains 2 - 15 at % Cr and 0.1 - 1.2 at. % Zr in order to improve the spallation resistance of the thermal barrier coating. Hence, claims 8 and 9 are not inventive. D6 teaches further, that after deposition of the β -NiAl layer and before deposition of the thermal barrier coating an anneal between 980 - 1090°C is carried out for two to four hours in a vacuum or an inert atmosphere such as Ar. Under these conditions traces of oxygen will be present. Therefore, also claim 12 is not inventive.

4.3. Claims 6 and 7 are not inventive, since D4 mentions already that Hf and Si additions improve the oxidation or corrosion resistance of the MCrAlY. A preferred MCrAlY composition contains 0 - 2 % Si and 0 - 1% Hf.

4.4. Claim 4 is not inventive, since D2 and D4 provide already coatings consisting of an MCrAlY layer and a thinner aluminide layer. Claim 4 is therefore considered as a mere variation of the teaching of D1. In addition, the skilled person knows how to adjust

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/07141

layer thicknesses to optimize physical properties, like e.g. stress. Finally, there is no surprising technical effect taught in the present application for the claimed relationship between the layer thicknesses.

4.5. It is known from D9 to reduce thermal stress in bond coatings by grading their composition along a direction perpendicular to the surface of the coating. D9 further discloses that the innermost layer may be an MCrAlY layer, whereas the outermost layers also contain Ni and Al. The skilled person, who wants to reduce the thermal stress in the bond layer of D1 would therefore consider the teaching of D9. Hence, claim 3 lacks inventive step.

4.6. Claim 10 is not inventive, since there are no surprising effects taught in the present application which the addition of Ti or Sc to the MCrAlY layer should have.

5. Industrial applicability

Claims 1 - 12 fulfill the requirement of industrial applicability, since subject-matter of present application can be made or used (in a technological sense) in industry (Article 33(4) PCT).

Re Item VII

Certain defects in the international application

The application does not comply with the provisions of Rule 5.1.a.ii PCT, because the most pertinent prior art, e.g. documents D1, D2, D5 and D9, are not cited and briefly discussed.

Re Item VIII

Certain observations on the international application

Clarity.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/07141

1. Parts of the description (page 3, line 1 - 4 and 8 - 14; page 6, line 22 - page 7, line 29; page 7, line 35 - page 8, line 20; page 8, line 25 - 34) teach to apply an outer layer, which is a MCrAlY layer having a γ -Ni phase structure. However, such a layer is not claimed, and is, hence, not a subject of the invention. Therefore, the respective parts of the description concerning such a layer need to be erased.

Moreover, this inconsistency is also represented in claims 7 (line 25) and 10 (line 8). For the same purpose, also Fig. 3 needs to be omitted, since it refers to another invention in which the intermediate and the outer layer consist of MCrAlY.

2. Claim 1 is not supported by the description in that its wording is different from what is taught under "Summary of the invention" on pages 2, line 30, - page 3, line 17. Further, there is a clear contradiction between what is said on page 3, line 20 - 21, and what is claimed. Claim 1 reads that the protective layer **consists of** an intermediate MCrAlY layer zone and an outer layer zone, i.e. two distinct layers, and not a single layer or a plurality of layers (page 3, line 16 - 17).

The subject-matter of the independent claims should be identical with what is taught in the part of the description usually referred to as "Summary of the Invention".

In addition it is not clear from the wording of the claim alone whether the Al content in line 16 and 17 refers to the Al content of the outer layer zone 19 or of the intermediate MCrAlY layer zone 16.

3. Claim 7: How can the yttrium being added and/or be partially replaced? Further it is unclear what is meant with "or the outer zone", because according to claim 1 the outer zone is not an MCrAlY layer.

4. Page 4, line 27 - 30, is unclear. What is meant by: A part of Y or in addition this MCrAlY layer zone 16 can also contain Hf, Zr, La, Ce or another Lanthanide? A part of Y always contains Y.

5. On page 5, line 17, it is stated that 21 - 37 wt. % Al correspond to 32 - 50 at. % Al. However, for a pure NiAl composition 21 - 37 wt. % Al correspond to 37 - 56 at. % Al.

claims

1. Highly oxidation resistant component (1),
having a substrate (4),
5 a protective layer (17),
which consists of
an intermediate MCrAlY layer zone (16) on or near the
substrate (4),
wherein M is at least one element out of the group Co,
10 Fe, Ni,
and an outer layer zone (19)
which is onto the intermediate MCrAlY layer zone (16),
which consists at least of the elements Ni and Al and
possesses the structure of the phase β -NiAl, and
15 whereby the Al content lays in the range between 21wt%
and 37wt%,
whereby the outer layer (19) contains further alloying
elements,
especially chromium and/or cobalt,
20 which do not destroy the phase β -NiAl.
2. Highly oxidation resistant component according to claim
1,
25 wherein the protective layer (17) consists of two
separated layers (16, 19).
3. Highly oxidation resistant component according to claim
30 1,
with a continuously graded concentration of the
composition of the intermediate and outer zone (16, 19)
inside the protective layer (17).

4. Highly oxidation resistant component according to claim 1,

wherein the outer layer zone (19) is thinner than the intermediate layer (16) on or near the substrate (4).

5

5. Highly oxidation resistant component according to claim 1,

10 wherein the intermediate MCrAlY-layer zone (16) has the composition (in wt%): 10% - 50% Co, 10% - 40% Cr, 6% - 15% Al, 0,02% - 0,5% Y, Ni base.

- 15 6. Highly oxidation resistant component according to claim 1,

wherein the intermediate MCrAlY-layer (16) or the outer layer zone (19) contains at least one further element such as (in wt%): 0,1% - 2% Si, 0,2% - 8% Ta or 0,2% - 5% Re.

20

7. Highly oxidation resistant component according to claim 1,

25 wherein the Yttrium of MCrAlY of the intermediate MCrAlY zone (16) or the outer zone (19) is added and/or at least partly replaced by at least one element out of the group Hf, Zr, La, Ce and/or other elements of the Lanthanide group.

30

8. Highly oxidation resistant component according to claim 1,

35 wherein the outer zone (19) is added at least one additional element out of the group Hf, Zr, La, Ce or other elements of the Lanthanide group.

9. Highly oxidation resistant component according to claim
8,
wherein the maximum amount of further additions is 1wt%.

5

10. Highly oxidation resistant component according to claim
1,
wherein the MCrAlY layer zone (16, 19) contains Ti
(Titanium) and/or Sc (Scandium).

10

11. Highly oxidation resistant component according to claim
1,
wherein on the outer layer zone (19) a thermal barrier
coating (13) is formed.

15

12. Highly oxidation resistant component according to claim
11,
wherein a heat treatment prior to applying a thermal
barrier coating is carried out
in an atmosphere with a low oxygen partial pressure,
especially at 10^{-7} and 10^{-15} bar.

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